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METHOD OF C₂H₄ DETECTION IN HUMID ATMOSPHERES USING A NANOPARTICULAR SnO₂ GAS SENSOR

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SUMMARY

Microhotplate architectures are widely studied in metal-oxide based sensors since their small size gives some advantages against traditional Taguchi type structures. The fast capability to vary sensors operating temperature allows to get information at different temperatures in short time periods and to extract transient information related to chemical adsorption and desorption processes. In this work, we present actual results in the development of a system, where a microhotplate architecture and synthesised nanoparticular SnO₂ like sensing material are used to identify ethylene (C₂H₄) in controlled humid atmospheres. Temperature modulation and Factorial Discriminant Analysis are used in the identification process. Low concentrations of C₂H₄ (0;1;2;5 ppm) have been identified in controlled high relative humidity ambiances.

Keywords: Tin oxide; gas sensor; temperature modulation; Factorial Discriminant Analysis.

Subject category: Chemical sensors and signal processing

INTRODUCTION

The use of metal-oxides gas sensors still being strongly limited because of their classical problems like signal drift and poor selectivity. However, different aspects of this kind of sensors still being studied to acquire a better knowledge of the sensing principles and to improve their actual performances. In addition to new materials and the use of additives to improve inner stability, sensitivity and selectivity, micromachined platforms came to reinforce the interest in metal-oxides, they present low power consumption with an interesting microelectronics fabrication compatibility.

In this work we present results obtained with a microhotplate architecture and nanosized sensing material developed by the Laboratory for Analysis and Architecture of Systems (LAAS-France) and the

Laboratory of Chemistry of Coordination (LCC-France) respectively. Our principal purpose is to develop a system for ethylene identification in humid atmospheres. Ethylene is an hormone who indicates plants maturity level and affects plants processes specially ripening stimulation; its supervision is really important for application in controlled fruits stocks and maturation chambers.

Sensor architecture and characteristic responses are presented. A method to reduce signal drifts and humidity influences is developed using transients responses to programmed temperature profiles. We show that transients responses to fast variations in operating temperature allows to extract enough useful information to be used in ethylene identification. Identification of low concentrations of ethylene in high and variable humidity ambiances has been possible using Factorial Discriminant Analysis and vector quantization.

ARCHITECTURE

The sensor is formed by a microhotplate platform and a nanoparticular SnO₂ sensing layer (Fig. 1). The microhotplate architecture was initially developed for Motorola and actually exploited by Microchemical Sensors S.A. A SiO_xN_y membrane of 1.5 μm supports a 600x430μm² polysilicon heater. Dimensions have been optimised to achieve good thermo-mechanical reliability[1].

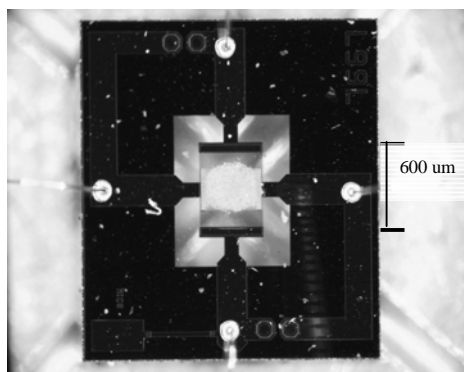


Fig. 1. Top view of the complete SnO₂ gas sensor

The heater can reach operation temperatures of 450°C with a power consumption of 90mW; its geometry was improved via numerical analysis to obtain a zone of high temperature homogeneity where the sensing layer must be placed. At the maximal temperature of operation (450°C) the heater electrodes are below 300°C, avoiding metal degradations (Design process details can be found in [2]).

The metal-oxide used in this sensor is a crystalline SnO₂ material synthesized by the decomposition and oxidation of a tin based organometallic precursor ([Sn(NMe₂)₂]₂). The average grain size obtained is about 20 nm of diameter [3]. This material is deposited by a drop deposition technique over the two electrodes placed in the homogeneous temperature region of the heater (Fig 1 and 2).

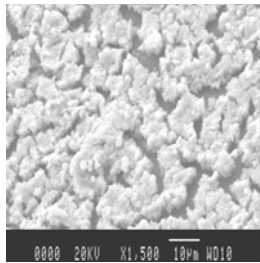


Fig. 2. SEM image of the sensing layer

Deposited material oxidation is made using the inner heater of each sensor. Three days aging (continued operation at 450°C) is needed to reach good material stability. Grain size and porous morphology are kept after oxidation.

SENSOR RESPONSE

The sensors were tested and characterized exhaustively by mean of a labView controlled experimental setup. Gas mixtures, flux levels, humidity and temperature can be fixed. Measuring and data acquisition can be realised with up to 16 sensors working at the same conditions.

Typical behaviour is found to different temperature isotherms in dry air: semiconductor like behaviour at low temperatures and an important decrease of conductivity at higher temperatures caused by a depletion zone increased by oxygen adsorption and ionisation. Slope changes in temperature are consistent with reported works [4].

The sensor operating at the physically maximum temperature in the heater (≈450°C) presents the highest sensitivity to ethylene (≈60% of resistance variation for 20 ppm of C₂H₄). Figures 3 and 4 show

experimental responses of a set of sensors for several C₂H₄ concentrations. In figure 3 we find the typical power law dependence of the resistance relative to gas concentrations $Rs = R_0 \cdot [C_2H_4]^\beta$, where β can be viewed like a sensitivity factor. This factor is dependant on the environment conditions and operation temperature, Ex. $\beta=0.43$ at 450°C in dry air.

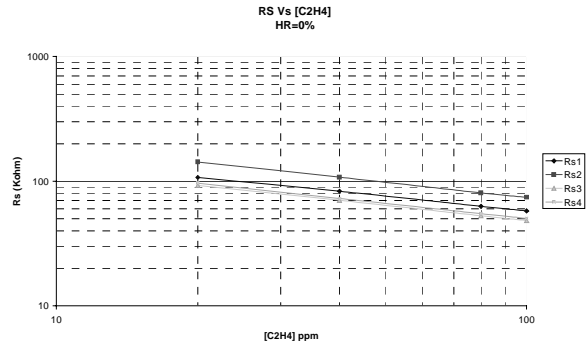


Fig. 3. Sensing material resistance Vs ethylene concentrations

Figure 4 shows a time response for cycled gas injection [0,1,10,10]ppm, where the essential reversibility and reproducibility characteristics can be observed.

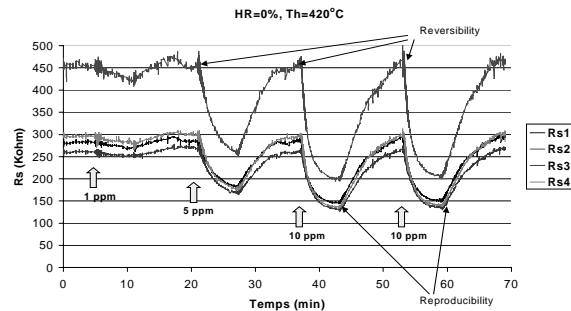


Fig. 4. Reversibility and Reproducibility

Unfortunately, this sensor doesn't escape to the principal problems of metal oxide sensors like signal drifts in the long term, cross sensitivity to others reducing gases and humidity dependencies. Low levels of relative humidity reduce abruptly the sensitivity (ex. Sensitivity to 20ppm of C₂H₄ decrease from 60% in dry air to 5% at 15% of RH).

SIGNAL PROCESSING

Temperature modulation is a relative new technique used to extract more useful information in the sensor response [5]. This fact is principally due to speed of adsorption and desorption of volatile species in the sensing layer which varies with the temperature and with the specie; also different kind of reactions can be exploited, like electronics transient, chemisorption transient, and temperature and humidity dependence.

Some works (ex.[6],[7]), show interesting results in gas measure and classification using different temperature profiles. It's reported that different gas signatures are obtained with programmed temperature sequences, then discrimination of gases and fixed mixtures with a single sensor are possible.

Performance improvement of our sensor by temperature modulation was easily tested. For example, with a simple cycled profile of temperature (10 seconds at 450°C followed by 10 seconds at 80°C) we obtain an important sensitivity increment from 5% to 35% in a 15% RH atmosphere, using like sensitivity the relation between the variations of the resistance at the highest temperature (eq. 1).

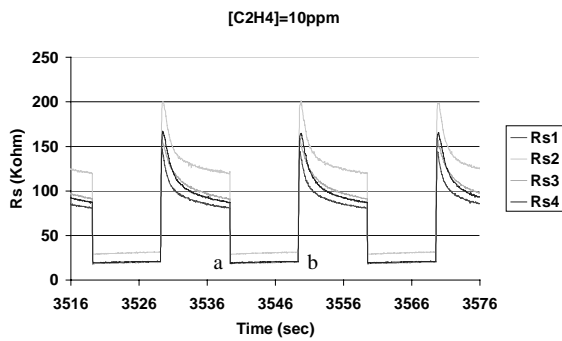


Fig 5. Cycled temperature response

$$\Delta R = a - b, S = \frac{\Delta R(xppm)}{\Delta R(0ppm)} \quad (1)$$

Variations in gas concentrations can be masked by humidity changes, rendering very difficult the gas quantization task. Since gas and humidity reactions in the sensing material are different processes, they affect sensor's response in particular ways (different constants ratios, activation energies, sensitivity influence, among others). These reactions have a big dependency on temperature, then fast changes in sensor operation temperature produce environment dependent transients responses. In this way, enough information to separate the humidity influence from gas response may be obtained with more complex temperature profiles. We have tested and optimised empirical profiles to detect low C₂H₄ concentrations in wet conditions. With a triangular stepped profile varying between 65 °C and 450 °C, good results have been obtained to classify 0, 1 and 5 ppm of C₂H₄ in fixed and opposite conditions (0 and 90% RH), (Fig. 6-8).

Principal Component Analysis (PCA) and Factorial Discriminant Analysis (FDA) methods were employed to reduce data and to make human observable (2D or 3D) the improvements reached with each profile. Better results have been achieved with FDA because of its supervised nature (pre-established classes).

The triangular profile was improved to keep minimal but sufficient variations caused by chemisorption processes, a 14 one-second steps profile with 55°C temperature difference between them was proposed. An input vector of 14 variables is obtained with the mean value of each step.

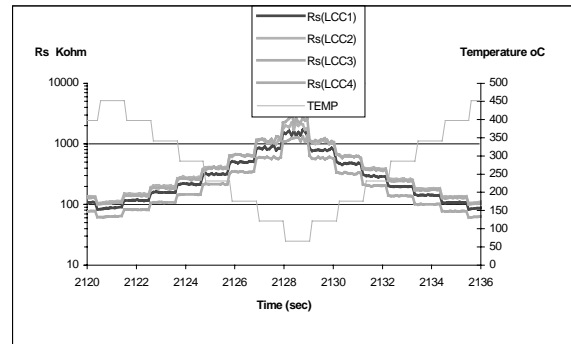


Fig. 6. Triangular temperature profile and sensors response

Each entry must be normalized in order to partially avoid drifts and sensors dissimilarities. Maximal value of resistance was used for normalisation with good results. Fig.7 shows four sensors normalised response to the triangular profile. 0 and 90% responses are clearly identifiable. Small but enough differences in ethylene responses are kept to produce a good differentiation via FDA, where the three concentrations (0, 1 and 5 ppm) of C₂H₄ were specified as predefined classes.

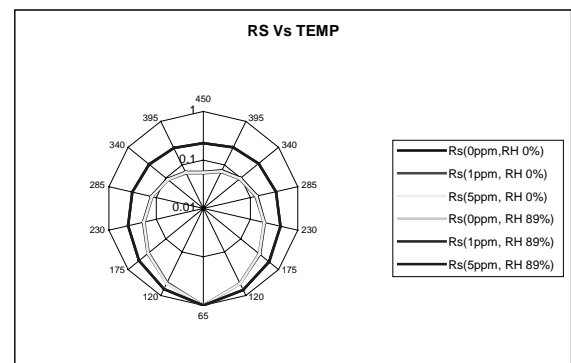


Fig. 7. Normalised temperature response at 0 and 90% of RH

FDA results showed that 100% of total variance was concentrated and likelihood distributed between the first two discriminant axes (Fig. 8). The three concentration levels specified can be clearly recognised. Linear Discriminant Analysis or Vectorial Quantization can be used to classify a pre-processed new entry.

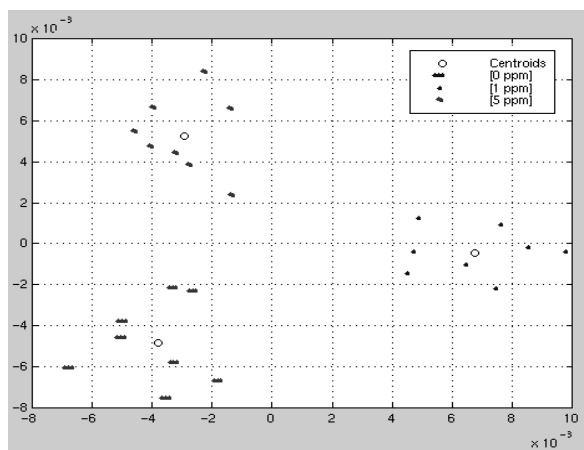


Fig 8. FDA for 0,1 and 5 ppm of C_2H_4 in 0 and 90% of RH.

In a more real context, humidity level is variable. Last procedure was tested with some modifications in high humid and variable ambiances. Correlation analysis between original data and the new subspace obtained via the FDA showed us that low temperature steps gave minimal contribution to total variance. A similar profile with 12 one-second steps with temperatures between 120°C and 450 °C was used to validate the proposed method in humidity controlled ambience with variable RH (80% ± 10%).

We have found that humidity variances mask the concentration variances for one sensor response, but by taking in to account the information of more than one sensors working at almost the same temperatures, we can obtain considerable improvements, as shown in figure 9, where the response of four sensors is used in the FDA analysis.

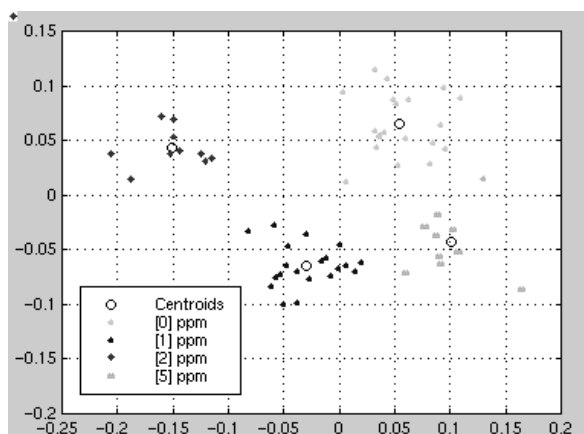


Fig. 9. FDA for 0,1,2 and 5 ppm C_2H_4 concentrations in 80 ± 10% of RH.

100% of variance is concentrated in three axes. First two axes give us a clear good identification with 74,7% of total variance. 60 of 120 entries have been used to find the translation matrix given by the FDA. 80% of total entries were well classified using vector

quantization, almost identical results have been found using Euclidean, Manhattan and L_∞ metrics.

CONCLUSIONS AND PERSPECTIVES

A new generation of gas sensors based on nanoparticular SnO_2 sensitive layer has been elaborated, tested and characterised. Good sensitivity to low concentrations of ethylene has been found, but it is significantly reduced in wet atmospheres. Desired identification of low concentrations of ethylene (0;1;2;5 ppm) in high and variable humid ambiances has been possible using modulated temperature and Factorial Discriminant Analysis.

A model of response in temperature, based on the electrochemical behaviour of the sensor including temperature and humidity effects is being optimised. A systematic optimisation approach of temperature profile is intended through this model.

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